Bernhard Welz
Michael Sperling

Atomic Absorption Spectrometry

Third, Completely Revised Edition

WILEY-VCH

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Preface to the third Edition

Atomic absorption spectrometry (AAS) is today, more than 40 years after it was proposed by Walsh as an analytical procedure, well established in numerous fields of instrumental analysis. Due to its high specificity and selectivity, as well as the fact that operation is relatively simple, AAS has gained its place alongside ICP OES and ICP-MS. It is used to perform numerous routine tasks in the laboratory ranging from the determination of trace contents through to major constituents. The fact that more than 1000 original papers dealing with AAS are published every year is a clear indication that there are numerous new developments over and above the routine applications.

These include new knowledge on atomization and other reaction mechanisms, improved analytical methods, especially in the fields of trace and ultratrace analysis, as well as in solids analysis, particularly using slurries. A major contribution has been the developments in instrumentation, such as transversely-heated graphite furnaces, integrated platforms, the application of solid-state detectors, or simultaneous multielement AAS, as well as new sample introduction and on-line pretreatment techniques such as flow injection. New areas of application including the analysis of 'high tech' materials and speciation analysis must also be mentioned.

To do justice to these manifold developments, this monograph has been rearranged, completely revised, and correspondingly extended. Thus, Chapter 1 on the historical development of AAS is new; in the first instance it demonstrates the maturity of the technique and provides the historically interested reader with the background information, and in the second instance it frees the technical chapters from historical ballast, leaving them free for a discussion of the current state of knowledge. Chapter 2 on the physical principles of AAS is also largely new; many of the topics discussed in this chapter are only inadequately treated in standard textbooks or not at all, and other topics have only been thoroughly developed in recent years.

Chapters 5, 6, and 7 are likewise new. Chapter 5 deals with procedures of measurement and calibration, the principles of quality control and assessment, and the basics of the statistical evaluation of the analytical results. Chapters 6 and 7 deal with automation and species analysis, and present a short review of the developments in these areas during recent years. On the other hand, the comparative chapter on other analytical procedures is no longer included since the recent developments in ICP OES and ICP-MS are well beyond the scope of this monograph.

Compared to the last edition, Chapter 8 includes significantly improved knowledge on the mechanisms of atomization and interferences, particularly for GF AAS and HG AAS. Chapter 9, dealing with the individual elements, now includes information on the stability and storage of test sample and calibration solutions, as well as the determination of species. In the treatment of applications in Chapter 10, methods no longer relevant, such as the determination of volatile elements by GF AAS using atomization from the tube wall with peak height evaluation, have been eliminated. On the other hand, all relevant procedures for speciation analysis are newly included.

Throughout this edition the terminology proposed by ISO and IUPAC has been used consistently. Thus, instead of ambiguous units such as ppm, ppb, etc., we have consistently used the ISO units mg/L, µg/L, ng/L and mg/g, µg/g, ng/g, etc. We have also attempted to avoid concentrations quoted in percent, which nevertheless was not possible in all cases since it was not clear from the original papers whether the concentration of acids, for example, were quoted in weight or volume percent.

To establish the bibliography we applied a relational databank (PELIDAS, © M. Sperling) to evaluate more than 55 000 entries from the field of atomic spectroscopy using plausibility checks to guarantee the quality of the citations. For the selection of the 6500 or so citations in this monograph, next to their information content, their topicality and availability also played a role. It is clear that for such a selection subjectivity comes into play, even though we have always attempted to be objective; we therefore ask for our readers' understanding if any paper that they deem to be important is not cited.

To maintain the topicality of this monograph we have also departed from traditional methods of production. Since the entire work, including the layout, was produced on the authors' PCs, we were able to update the contents until shortly before publication. We feel sure our readers will excuse the inadequacies of the word processor used in producing the layout since these are more than compensated by the advantage of topicality.

Überlingen, September 1998

Bernhard Welz
Michael Sperling

Preface to the second Edition

In the nine years since the publication of the first edition of this monograph, atomic absorption spectrometry has undergone a remarkable development. This is perhaps no entirely true for flame AAS, which nowadays is established as a routine procedure in all branches of elemental analysis, but it is certainly the case with all other techniques of AAS. Even though flame AAS had already found acceptance in many standard methods due to its reliability in the mg/L range, it is only a few years ago that considerable doubt was cast on the ability of graphite furnace and hydride generation AAS to provide correct results at all in the µg/L and ng/L ranges.

The difficulties observed by many analysts using these techniques were due in part to the shortcomings of the instruments employed and in part to non-optimum application, since the significance of a number of parameters had not been recognized. In addition, the general problems of trace and nanotrace analysis had to be taken into consideration, since these newer techniques opened this concentration range to AAS.

These days, the causes of the majority of interferences and also the possibilities for their elimination are known. Even if all technical problems have not been completely solved, the way to their solution has been shown.

Thus, as well as the flame technique, the graphite furnace, hydride generation, and cold vapor techniques are nowadays of equal significance. The major field of application of these newer techniques is in trace, nanotrace and ultratrace analysis. Each of these techniques has its own atomizer, its own specific mechanisms of atomization and interference, and of course its own preferred field of application. In this second edition, these three techniques are thus treated separately whenever this appears expedient.

This made it necessary to substantially revise numerous chapters. Chapter 3 now deals only with atomizers, their historical development, and their specific characteristics for each technique. A new chapter 8 has been introduced in which the mechanisms of atomization and the interferences for each technique are discussed in detail. Additionally, typical interferences and their elimination are mentioned. A general discussion and classification of interferences is presented in chapter 7. Application of the Zeeman effect for background correcttion is also treated in detail in this chapter. This treatment includes the theoretical aspects of the method, the various configurations, and their advantages and disadvantages. In the chapters on individual elements and specific applications, the various techniques are, wherever applicable, weighed against each other.

A discussion on trace and nanotrace analysis has also been newly introduced, since the newer techniques of AAS are among the most sensitive methods for elemental analysis. Solids analysis is also treated since this has become possible with the graphite furnace technique. A section on environmental analysis has been included in the chapter on specific applications, and topical questions on the analysis of air, waste water and sewage sludge are addressed.

Among associated analytical methods, atomic emission spectrometry employing an inductively coupled argon plasma is discussed especially, since it is frequently regarded as a competitive technique to flame AAS. However, a broad treatment of this theme is outside the scope of this book.

Graphite furnace atomic emission spectrometry has also received attention even though, like atomic fluorescence spectrometry, it is rarely used in practice.

Finally, terms, nomenclature and units of measurement have been brought into line with the latest international standards – a fact reflected in the changed title of this monograph. Of particular help in this respect was my work on the committee of material testing within the German Institute of Standardization. This committee was chaired by Dr. Hans Massmann, who, until his death, worked on the completion of DIN 51 401 and who also made valuable suggestions for the second edition of this book – a fact greatly appreciated.

I should also like to thank those readers who wrote to me pointing out errors in the first edition; they have made valuable contributions to improving this work. I should particularly like to thank Sir Alan Walsh who drew my attention to a number of errors and who proposed numerous improvements and more precise definitions.

The numerous new diagrams were prepared with the customary care by Mr. E. Klebsattel who receives my grateful thanks. I should also like to thank Mr. J. Storz for designing the cover.

This book is the English-language version of its German forerunner "Atomabsorptionsspektrometrie" (formerly "Atom-Absorptions-Spektroskopie") which is now in its third edition. As for the first edition the translation has been very capably carried out by Christopher Skegg to whom I extend my thanks.

Meersburg, May 1985 Bernhard Welz

Preface to the first Edition

It was very convenient that the translation of my book into the English languagee was undertaken just as I was completing the second German edition. Therefore, all the latest developments and publications could be incorporated directly in the English edition

Usually, years go by between the publication of the original book and the completion of a translation which, therefore, typically does not represent the latest state. Here, however, the translation could be published about a year after the original German edition. This is of special importance for the rapidly growing field of furnace atomic absorption which was hardly known a few years ago when the first edition of my book was published. In the meantime it has found worldwide acceptance among analysts.

So, to all my friends and colleagues who have been involved in the translation and completion of this book, I would like to express my thanks for the time that they have spent and for all the effort that they have put into it so that it could be published so early. Last not least, I want to express my pleasure that my book on Atomic Absorption Spectroscopy has been accepted for translation into English. I hope that it will prove a stimulus to atomic absorption spectroscopy and will help analysts and spectroscopists in their daily work.

Meersburg, March 1976 Bernhard Welz

Contents

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Abbreviations and Acronyms

The following abbreviations and acronyms are used in this monograph:

AA	acetylacetone
AAS	atomic absorption spectrometry
A/D (conversion)	analog-to-digital
AES	Auger electron spectroscopy
AFM	atomic force microscopy
ANOVA	analysis of variance
APDC	ammonium pyrrolidine dithiocarbamate
AsB	arsenobetaine
ASV	anode stripping voltammetry
BC	background correction; background corrector
BCR	Bureau Commun de Référence, Belgium
BERM	International Symposium for Biological and Environmental Reference Materials
BG	borosilicate glass
BOC	baseline offset correction
BPTH	1,5-bis[phenyl-(2-pyridyl)methylene]thiocarbohydrazide
CARS	coherent anti-Stokes Raman spectroscopy
CCD	charge coupled device
CE	concentration efficiency
CF	continuous flow
CGC	capillary gas chromatography
CI	consumptive index
CID	charge injection device
CPG	controlled pore glass
CRA	carbon rod atomizer
CRM	certified reference material
CSIRO	Commonwealth Scientific and Industrial Research Organization (Australia)
CT	cryotrapping
CV AAS	cold vapor AAS
DAL	dialkyl-lead
DBT	dibutyltin
DCTA	1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid
DDAB	didodecyl-dimethylammonium-bromide
DDC	diethyldithiocarbamate
DDTC	diethyldithiocarbamate
DDTP	dimethoxydithiophosphate
DESe	diethylselenium
DIBK	di-isobutyl ketone
DIN	*Deutsches Institut für Normung* (German Standards Institute)

DMA	dimethylarsonate
DMF	dimethylformamide
DMSe	dimethylselenium
DMSO	dimethylsulfoxide
DPTH	1,5-bis(di-2-pyridylmethylene)thiocarbonhydrazone
DTC	dithiocarbamate
DTP	dithiophosphoric acid
EDL	electrode discharge lamp
EDTA	ethylendiamine-tetraactic acid
EDX	energy-dispersive X-ray spectrometry
EF	enrichment factor
EG	polycrystalline electrographite (also *Erfassungsgrenze* in Section 5.2.3)
EMP	electron microprobe
EPA	Environmental Protection Agency (U.S.A.)
ESCA	electron spectroscopy for chemical analysis
ET AAS	electrothermal AAS
ETV	electrothermal vaporization
ETV-ICP-MS	electrothermal vaporization inductively coupled plasma mass spectrometry
F AAS	flame AAS
FANES	furnace atomic non-thermal excitation spectrometry
FEP	fluorinated engineering polymers (perfluoro-ethylene-propylene)
FG	flint glass
FI	flow injection
FIA	flow injection analysis
FID	flame ionization detector
FIMS	flow injection mercury system (Perkin-Elmer)
FIT	flame-in-tube (non-heated quartz tube atomizer with flame)
FWHM	full width at half maximum
GAP	good analytical practice
GC	gas chromatography (also glassy carbon in Chapter 1)
GF AAS	graphite furnace AAS
GLP	good laboratory practice
GLS	gas-liquid separator
HCL	hollow cathode lamp
HG AAS	hydride-generation AAS
HGA	longitudinally-heated graphite atomizer (Perkin-Elmer)
HMA-HMDTC	hexamethyleneammonium-hexamethylenedithiocarbamate
HMDTC	hexamethylenedithiocarbamate
HPLC	high performance liquid chromatography
IAEA	International Atomic Energy Authority (Austria)
IBMK	isobutyl methyl ketone
ICP	inductively coupled plasma
ICP-MS	inductively coupled plasma mass spectrometry

ILOD	instrument limit of detection
INAA	instrumental neutron activation analysis
IR	infrared (wavelength range > 800 nm)
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
KR	knotted reactor
LC	liquid chromatography
LD-TOF-MS	laser-dispersion time-of-flight mass spectrometry
LEAFS	laser-enhanced atomic fluorescence spectrometry
LOD	limit of detection
LOQ	limit of quantitation
MBT	monobutyltin
MeHg	methylmercury
MeT	methyltin
MIP	microwave induced plasma
MMA	monomethylarsonate
MMT	monomethyltin
MS	mass spectrometry
NAA	neutron activation analysis
NaHEDC	bis(2-hydroxyethyl)dithiocarbamate sodium salt
NIST	National Institute of Standards and Technology (U.S.A.)
NL	non-linearity
NTA	nitrilotriacetic acid
OES	optical emission spectroscopy
PAN	1-(2-pyridylazo)-2-naphthol
PAR	4-(2-pyridylazo)resorcinol
PC	polycarbonate
Pd-Mg	mixed modifier of palladium nitrate and magnesium nitrate
PE	polyethylene
PET	poly(ethyleneterephthalate)
PFA	perfluoroalkoxy plastics
PG	pyrolytic graphite
PI	polyimides
PIXE	particle [proton] induced X-ray emission spectroscopy
PMPB	1-phenyl-3-methyl-4-benzoyl-5-pyrazolone
PMT	photomultiplier tube
PP	polypropylene
PSF	polysulfone
PTFE	polytetrafluoroethylene
PU	polyurethane
PVC	polyvinyl chloride
PVD	physical vapor deposition
QF	quartz tube furnace with a small flame burning in it
QTA	quartz tube atomizer
RBS	Rutherford backscattering spectroscopy

REE	rare earth elements
RF	radio frequency
RNAA	radiochemical neutron activation analysis
ROC (model)	reduction of oxides by carbon
S	silica
S-H	Smith-Hieftje high current pulsing background correction
S/N	signal-to-noise ratio
SEM	scanning electron microscopy
SeMet	selenomethionine
SIMS	secondary ion mass spectrometry
SRM	standard reference material
SS	solid sampling
SSD	solid state detector
SSF	spectral shadow filming
STM	scanning tunneling microscopy
STPF	stabilized temperature platform furnace (a concept for quasi isothermal atomization)
TAL	tetraalkyl-lead
TAR	4-(2-thiazolylazo)resorcinol
TBT	tributyltin
TEL	tetraethyl-lead
TEM	transmission electron microscopy
TGL	temperature gradient lamp
THF	tetrahydrofuran
THGA	transversely-heated graphite atomizer with integrated platform (Perkin-Elmer)
TMDTC	tetramethylenedithiocarbamate
TML	tetramethyl-lead
TMSe	trimethylselenonium
TOMA	tri-N-octylmethylammonium
TOPO	trioctylphosphine oxide
TPG	total pyrolytic graphite
TPN (patients)	total parenteral nutrition
TPP	triphenylphosphine
TTFA	thenoyltrifluoroacetone
UV	ultraviolet (wavelength range < 400 nm)
WHO	World Health Organization
XAD	ion exchange resin
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction analysis
ZBC	Zeeman-effect background correction

'Atomic absorption spectrometry (AAS) is a spectroanalytical procedure for the qualitative detection and quantitative determination of elements employing the absorption of optical radiation by free atoms in the gaseous state' [1501].

1 The Historical Development of Atomic Absorption Spectrometry

1.1 The Early History

The beginning of optical spectroscopy is generally attributed to Sir ISAAC NEWTON [3205] who, in a letter to the Royal Society in 1672, described the observation that sunlight is split into various colors when it is passed through a prism. Albeit JOANNES MARCUS MARCI VON KRONLAND (1595–1667), professor of medicine at the University of Prague (Figure 1-1), had already explained the origin of the rainbow on the basis of the diffraction and scattering of light in water droplets in his book *Thaumantias. Liber de arcu coelesti deque colorum apparentium natura ortu et causis* published in 1648; he can thus be looked upon as the first spectroscopist.

The history of absorption spectrometry is closely connected with the observation of sunlight [5934]. In 1802 Wollaston discovered the black lines in the sun's spectrum. These were later investigated in detail by Fraunhofer, who assigned letters to the

Figure 1-1. 'Joannes Marcus Marci, Doctor of Philosophy and Medicine, and Professor, born in Kronland in Bohemia, 17 June 1595.'

strongest lines, starting at the red end of the spectrum with the letter A. Even nowadays it is common to refer to the 'sodium D line', a designation originated by Fraunhofer.

In 1820 Brewster expressed the view that these Fraunhofer lines were caused by absorption processes in the sun's atmosphere. The underlying principles of this absorption were established by KIRCHHOFF and BUNSEN [3121–3124] during their systematic examination of the line reversal in the spectra of alkali and alkaline-earth elements. They conclusively demonstrated that the typical yellow line emitted by sodium salts in a flame is identical to the black D line of the sun's spectrum. The classical experimental arrangement is shown in Figure 1-2.

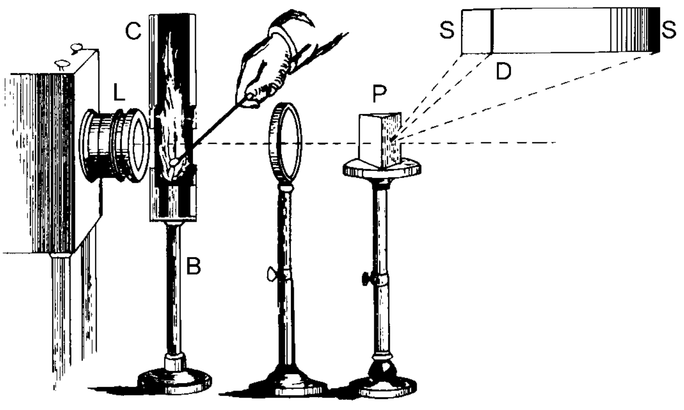

Figure 1-2. Experimental setup of KIRCHHOFF and BUNSEN for investigating the line reversal in the sodium spectrum (according to [5934]). Radiation from a lamp is focused by lens **L** through the flame of a Bunsen burner **B** into which sodium chloride is introduced with a spatula. The radiation beam is dispersed by prism **P** and observed on screen **S**. The sodium D line appears as a black discontinuity in the otherwise continuous spectrum.

The relationship between emission and absorption was formulated by Kirchhoff in his law, which is generally valid and states that any material that can emit radiation at a given wavelength will also absorb radiation of that wavelength.

The connection between atomic structure and the interaction of atoms with radiation was established by Planck (1900) in the quantum law of absorption and emission of radiation, according to which an atom can only absorb radiation of well defined wavelength λ or frequency ν, i.e. it can only take up and release definite amounts of energy ε:

$$\varepsilon = h\nu = \frac{hc}{\lambda}, \tag{1.1}$$

where h is Planck's constant and c is the speed of light. Characteristic values of ε and ν exist for each atomic species.

On the basis of this and many other spectroscopic observations, Bohr proposed his atomic model in 1913, the fundamental principle of which is that atoms do not exist in random energy states, but only in certain fixed states which differ from each other by integral quantum numbers. Upon absorbing a quantum of energy, an atom is transformed into a particular, energy-enriched state 'containing' the radiation energy which has been taken up. After a period of around 10^{-9} s to 10^{-8} s the atom can re-emit this energy and thus return to the ground state.

Although Kirchhoff had already recognized the principle of atomic absorption in 1860 and the theoretical basis was steadily extended during the following decades, the practical significance of this technique was not recognized for a long time. Since the work of Kirchhoff, the principle of atomic absorption was mainly used by astronomers to determine the composition and concentration of metals in the atmospheres of stars. Chemical analyses were only carried out very sporadically by this technique; the determination of mercury vapor did, however, acquire a degree of importance [4225, 6380] (see Section 1.8.1).

The actual year of birth of modern AAS was 1955. In that year, publications authored independently by WALSH [6135] and ALKEMADE and MILATZ [125, 126] recommended AAS as a generally applicable analytical procedure.

1.2 Sir Alan Walsh and the Period 1952–1962

Even though the publications by ALKEMADE and MILATZ [125, 126] in The Netherlands and WALSH [6135] in Australia appeared in the same year, making it difficult to answer the question as to who actually rediscovered AAS, Alan Walsh (Figure 1-3) is generally recognized as the 'father' of modern AAS. This privilege is his just due since he campaigned with untiring energy against the resistance to this new idea for more than a decade, spending much time to overcome the disinterest and misunderstanding. Best of all, let Alan Walsh himself describe the events and developments of the period 1952 to 1962 [6137].

'My initial interest in atomic absorption spectroscopy was a result of two interacting experiences: one of the spectrochemical analysis of metals over the period 1939–1946; the other of molecular spectroscopy over the period from 1946–1952. The interaction occurred early in 1952, when I began to wonder why, as in my experience,

Figure 1-3. Sir Alan Walsh.

molecular spectra were usually obtained in absorption and atomic spectra in emission. The result of this musing was quite astonishing: there appeared to be no good reasons for neglecting atomic absorption spectra; on the contrary, they appeared to offer many vital advantages over atomic emission spectra as far as spectrochemical analysis was concerned. There was the attraction that absorption is, at least for atomic vapours produced thermally, virtually independent of the temperature of the atomic vapour and of excitation potential. In addition, atomic absorption methods offered the possibility of avoiding excitation interference, which at that time was thought by many to be responsible for some of the interelement interferences experienced in emission spectroscopy when using an electrical discharge as light source. In addition, one could avoid problems due to self-absorption and self-reversal which often make it difficult to use the most sensitive lines in emission spectroscopy.'

'As far as possible experimental problems were concerned, I was particularly fortunate in one respect. For several years prior to these first thoughts on atomic absorption, I had been regularly using a commercial i.r. spectrophotometer employing a modulated light source and synchronously tuned detection system. A feature of this system is that any radiation emitted by the sample produces no signal at the output of the detection system. This experience had no doubt prevented the formation of any possible mental block associated with absorption measurements on luminous atomic vapours.'

In an internal report for the period February–March 1952 Walsh suggested that the same type of modulated system should be considered for recording atomic absorption spectra. 'Assuming that the sample is vaporised by the usual methods, e.g. flame, arc, or spark, then the emission spectrum is "removed" by means of the chopper principle. Thus the emission spectrum produces no output signal and only the absorption spectrum is recorded.'

In the same report he continued: 'For analytical work it is proposed that the sample is dissolved and then vaporised in a Lundegardh flame. Such flames have a low temperature (2000 K) compared to arcs and sparks (5000 K) and have the advantage that few atoms would be excited, the great majority being in the ground state. Thus absorption will be restricted to a small number of transitions and a simple spectrum would result. In addition, the method is expected to be sensitive since transitions will be mainly confined to those from the ground level to the first excited state.'

The next report for the period April–May 1952 included the diagram shown in Figure 1-4 and described the first experiment as follows: 'The sodium lamp was operated from 50 cycles/s and thus had an alternating output so that it was not necessary to use a chopper. The D lines from the lamp were isolated—but not resolved from each other—by means of a direct vision spectroscope and their intensities were measured by means of a photomultiplier tube, the output from which was recorded on a cathode ray oscillograph. Amplification of the signal was achieved by the a.c. amplifiers in the oscillograph. With the slit-width used the signal gave full-scale deflection on the oscillograph screen. A Meker flame was interposed between the sodium lamp and the entrance slit of the spectroscope. When a solution of sodium chloride was atomised into the air supply of the flame the signal at the oscillograph was reduced to zero. The principle of the method is therefore established.'

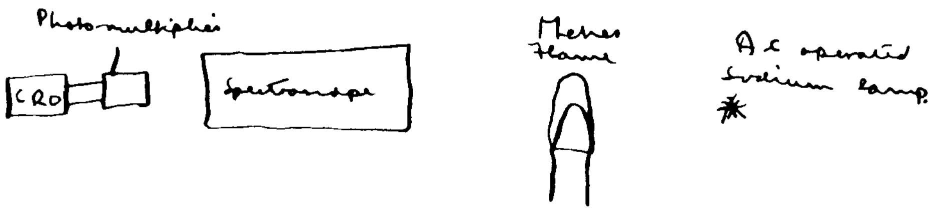

Figure 1-4. The first outline by Walsh for the measurement of atomic absorption from his report for April–May 1952.

In retrospect Walsh admitted to 'optimistic naivety'; he nevertheless recalls: 'This simple experiment gave me a great thrill, and I excitedly called John Willis, who at the time was working on infrared spectroscopy and was later to make important contributions to the development of atomic absorption methods of chemical analysis. "Look," I said, "that's atomic absorption." "So what?" was his reply, which was the precursor of many disinterested reactions to our atomic absorption project over the next few years.'

In his report for June–July 1952 Walsh discussed the problem of recording atomic absorption spectra using a continuum source and came to the conclusion that a resolution of approximately 2 pm would be required. This was far beyond the capabilities of the best spectrometer available in his laboratory at that time. The report concluded: 'One of the main difficulties is due to the fact that the relations between absorption and concentration depend on the resolution of the spectrograph, and on whether one measures peak absorption or total absorption as given by the area under the absorption/wavelength curve.'

This realization led him to conclude that the measurement of atomic absorption requires line radiation sources with the sharpest possible emission lines. The task of the monochromator is then merely to separate the line used for the measurement from all the other lines emitted by the source. The high resolution demanded for atomic absorption measurements is in end effect provided by the line source.

At this point Walsh had already recognized the salient points of AAS: The use of line radiation sources, which make a high-resolution monochromator unnecessary, the principle of modulation, which makes the technique selective and eliminates the radiation emitted by the atomizer, and the use of laminar flames of relatively low temperature to atomize the sample. A patent for the technique was lodged at the end of 1953 and an atomic absorption spectrometer was publicly demonstrated in Melbourne in March 1954. However, during the exhibition the instrument aroused little interest.

The last changes to the specifications for the patent were submitted in October 1954 and immediately thereafter WALSH sent his first manuscript about AAS to Spectrochimica Acta, which was published at the beginning of 1955 [6135]. This paper was followed by others from Walsh's group [5010] and also from ALLAN [135] in New Zealand and DAVID [1426] in Australia. Nevertheless the technique was still looked upon as a 'scientific curiosity' rather than a practical analytical technique.

In the meantime, Hilger and Watts had built an instrument, but since the radiation source was not modulated it could not exploit the technique. Other manufacturers later made the same mistake. WALSH [6137] recalls that 'by 1958 there was no sign of any instrument manufacturer willing to produce the type of instrument which we thought desirable.'

WALSH then decided to arrange for the production of appropriate equipment. The necessary items were manufactured by three small companies in Melbourne and then assembled by the user. 'As it transpired,' he wrote [6137], 'for the next few years the members of our research group were increasingly involved in supporting the commercial production in Australia of atomic absorption equipment. That a new type of Australian industry was eventually created was, of course, cause for much satisfaction, but it was inevitable that there was a substantial reduction in our research effort over a period of several years.'

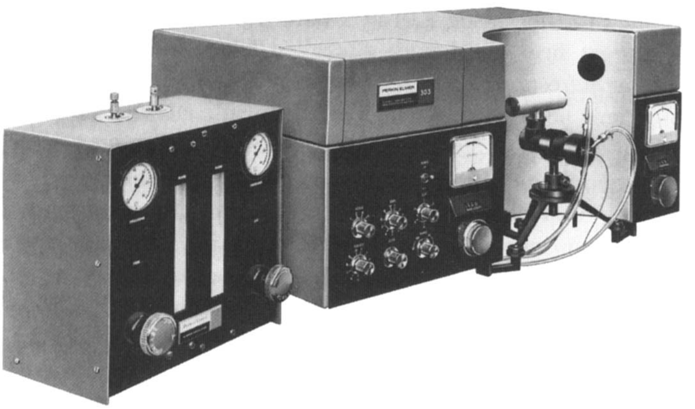

Figure 1-5. The Perkin-Elmer Model 303, the first spectrometer built exclusively for AAS.

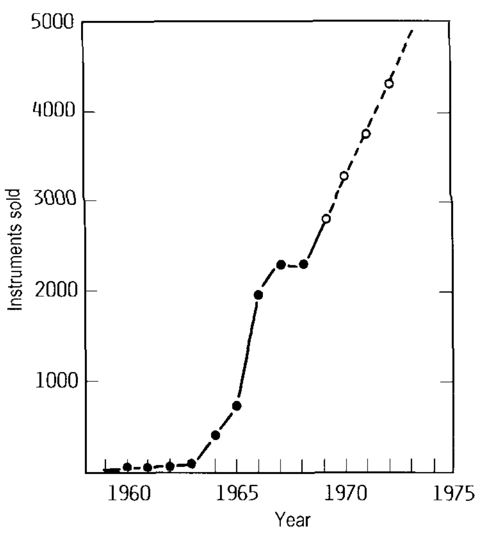

Figure 1-6. Sales figures for atomic absorption spectrometers during the first 15 years (from [6138]).